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The synthesis, characterisation, X-ray structure and magnetism of dinuclear-based bis[μ-(1,1,3,3-tetracyano-2-ethoxypropenido-κ^2*N,N'*) (1,1,3,3-tetracyano-2-ethoxypropenido-κ*N*)(2,2'-bipyridine)copper(II)] organized in alternating chains via semi-coordinating Cu-N distances.

Abderazzak Addala[a], Fatima Setifi[a,*], Konstantin G. Kottrup[b], Christopher Glidewell[c,*], Zouaoui Setifi[a,d], Graham Smith[e], Jan Reedijk[b,f,*].

[a]*Laboratoire de Chimie, Ingénierie Moléculaire et Nanostructures (LCIMN), Université Ferhat Abbas Sétif 1, Sétif 19000, Algeria.*

[b]*Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands.*

[c]*School of Chemistry, University of St Andrews, Fife KY16 9ST, United Kingdom.*

[d]*Département de Technologie, Faculté de Technologie, Université 20 Août 1955-Skikda, Skikda 21000, Algeria.*

[e]*Science and Engineering Faculty, Queensland University of Technology, GPO Box 2434, Brisbane, Qld 4001, Australia.*

[f]*Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia.*

Abstract:

The monoanionic ligand 1,1,3,3-tetracyano-2-ethoxypropenide (tcnoet) is reported with its Cu(II)–bpy complex of formula $[Cu_2(\mu\text{-tcnoet})_2(tcnoet)_2(bpy)_2]$. The structure has been determined using X-ray diffraction and features an alternating chain with bridging tcnoet ligands. One ligand acts as a bidentate, dinucleating ligand with one short Cu–N and one medium Cu–N bond, whereas the other tcnoet is largely monodentate, albeit with a very weak interdimer Cu–N bond. Despite the arrangement in dinuclear units, further arranged into linear chains through the non-bridging tcnoet ligand, the compound shows no significant magnetic exchange, as deduced from magnetic susceptibility down to 4 K. Ligand-field, IR and EPR spectra in the solid state and in frozen solution are reported and are consistent with the overall structure.

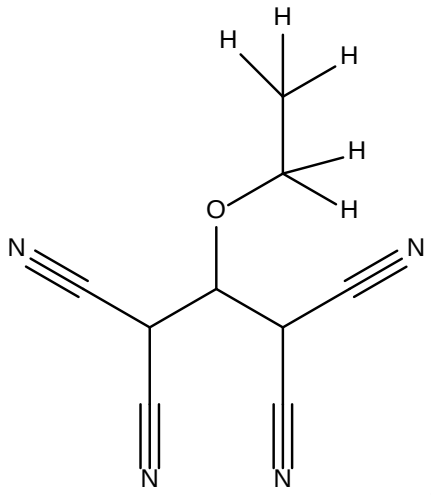
Key words: Copper(II) coordination chemistry; 1,1,3,3-tetracyano 2-ethoxypropenide; Magnetism; X-ray diffraction; EPR

Highlights: See separate file

TOC/Graphabs: See separate files

Introduction

Polycyano species, such as TCNQ **[**(2,5-cyclohexadiene-1,4-diylidene) -dimalononitrile, 7,7,8,8-tetracyanoquinodimethane, also known as tetracyanoquinodimethane**]** and tetracyanoethene [TCNE], are well known [1-8], as well as many derivatives of them, some containing additional groups [3, 9-18]. A recent example is 1,1,3,3-tetracyano-2-ethoxypropenide (tcnoet), see scheme 1.



Scheme 1: Schematic structure of the tcnoet monoanion.

The presence of CN groups makes these anionic species potential ligands for metals, although binding, if present, is often weak [10]. Copper(II) is a metal ion that is known to accept both short and long M-L bonds, and therefore it appeared to be of interest to see whether mononuclear or polymeric compounds were formed with this ligand. To generate soluble products 2,2'-bipyridine (bpy) was added as a co-ligand.

The present study deals with a unique compound with the anionic ligand 1,1,3,3-tetracyano(2-ethoxy)propenide [10], abbreviated tcnoet, in which the ligand is involved in two different binding modes when complexed with Cu^{II}.

Experimental part

2.1. Starting materials

Copper(II) chloride dihydrate, 2,2'-bipyridyl and solvents were used as commercially available. The potassium salt of tcnoet was prepared by reaction in ethanol of 1,1-diethoxy-2,2-dicyanoethene with malononitrile and potassium *t*-butoxide as described in the literature [10]. Anal. Calc. for $KC_9H_5N_4O$: C, 48.20; H, 2.25; N, 24.98; K, 17.43. Found: C, 47.99; H, 2.24; N, 25.20; K, 17.52%. IR data (KBr, v/cm^{-1}): 3427br, 2205s, 1647w, 1499s, 1425m, 1379m, 1348m, 1187m, 999m.

2.2. Synthesis of the Cu compound (1)

Under aerobic conditions, an ethanolic solution (5 mL) of 2,2'-dipyridyl (50 mg, 0.32 mmol) was added, with stirring at room temperature to an aqueous solution (5 mL) of $CuCl_2 \cdot 2H_2O$ (54.56 mg, 0.32 mmol). After 10 min, a 25 mL aqueous solution of Ktcnoet (144 mg, 0.64 mmol), was added and the resulting mixture was stirred for 1 h at room temperature. Upon standing at room temperature, deep green crystals appeared, which were collected by filtration, and from which a crystal suitable for X-ray diffraction was selected.

Elemental Anal. for $C_{56}H_{36}Cu_2N_{20}O_4$: Calc.: C, 56.99; H, 3.07; N, 23.73. Found: C, 56.91; H, 3.04; N, 23.69%.

2.3. Spectroscopy and magnetism

Infrared spectra were recorded using routine equipment in the range 3500-500 cm^{-1}. Ligand field spectra were performed on solid powders (room T, diffuse reflectance mode) in the range 200-1100 nm. EPR spectra were recorded at X band frequencies on the solid powder at room temperature, and also in frozen MeOH solution.

Magnetic susceptibility measurements on the solid product were recorded on a Quantum Design MPMS-XL SQUID magnetometer. DC magnetization measurements were performed in a field of 0.1 T, from 4 to 300 K (heating mode) with a rate of ± 0.3-1.1 $Kmin^{-1}$.The measuring time was 20 h; corrections for the diamagnetism were calculated using Pascal's constants; the TIP (temperature independent paramagnetism) correction was used as 0.00085 emu/Cu.

2.4. X-ray diffraction and refinement

A suitable single crystal study of $[Cu_2(\mu\text{-tcnoet})_2(tcnoet)_2(bpy)_2]$ was performed at 296 K on a Bruker–Nonius X8 ApexII diffractometer equipped with a CCD area detector by using graphite-monochromated Mo *K*α radiation (λ = 0.71073 Å) generated from a sealed tube source. Data collection, indexing with reduction and absorption corrections were performed using APEX2, SAINT and SADABS programs, respectively [19]. The structure was solved by direct methods and refined by full-matrix least-square procedure based on F^2 using the SHELX package [20]. All hydrogen atoms bound to carbon were included in the model at geometrically calculated positions and refined using an appropriate riding model. Hydrogen atoms bound to nitrogen or oxygen were located from a difference Fourier map and refined using appropriate geometrical restraints.

Crystallographic data: $C_{56}H_{36}Cu_2N_{20}O_4$, triclinic, *P*-1, *a* =8.9200(2), *b* = 12.0921(3), *c* = 12.8264(3) Å, α = 98.691(2), β = 92.562(3), γ = 98.285(2)°, *V* = 1350.19(6) $Å^3$, *Z* = 2; D_{calc} = 1.451 g cm^3; crystal: a deep green block with dimensions 0.41 x 0.36 x 0.27 mm. A total of 46053 reflections were measured, of which 7860 were independent. R_{int} = 0.0408, Dataset (*hkl*) = -12:12; -17:17; -18:18, parameters/restraints = 372/0. Refinement of F^2, against all reflections, led to

R(F)[$I > 2\sigma(I)$] = 0.0379, , $R_w(F^2)$ = 0.0960, S = 1.023, minimum and maximum residual density (e Å^{-3}) = -0.433, 0.419.

3. Results and discussion

3.1. Physical measurements

The IR spectrum of the title compound presents two strong absorption bands (2205 and 2236 cm^{-1}) assignable to the v(CN) vibration. The first band is similar to that observed in the potassium salt K(tcnoet) spectrum and containing the weakly coordinated tcnoet moiety (2205 cm^{-1}), while the second is slightly shifted to higher wave-numbers, typical for stronger coordinated CN groups. This is in good agreement with the presence of both coordinated and uncoordinated CN groups in the compound as shown by the X-ray structure (see below). The spectrum has been redrawn in Figure S1.

The solid-state diffuse reflectance spectrum shows a broad band at 660 nm, assigned as the Cu *d-d* transition, and two higher energy bands assigned to Cu-L charge transfer at 480 nm and 355 nm. The spectrum has been redrawn in Figure S2.

The frozen-solution EPR in MeOH, shows a clear signal, with hyperfine splittings on $g_{//}$, having values for $g_{//}$ and $A_{//}$ of 2.30 and 150 Gauss. These values agree with mononuclear Cu(II) with a N/O donor set of ligands, and implies a breakup into mononuclear species in MeOH, likely partly solvated by MeOH. The spectrum has been redrawn in Figure S3.

As a solid the powder EPR at room T shows a shoulder at $g_{//}$ = 2.25 and a maximum at g = 2.06; upon cooling to 77 K the $g_{//}$ signal sharpens to a single band with $g_{//}$ 2.26, but hyperfine splitting for Cu^{II} is not resolved. The spectrum has been redrawn in Figure S4. This pattern agrees with the structure, where the Cu(II) ions are not too far separated and weakly bridged by ligands.

To investigate whether or not in the solid state significant magnetic Cu-Cu interactions occur, the powder magnetic susceptibility was recorded down to very low T (4 K). It was found, however, that the magnetic moment remained about 1.8 BM and that no significant changes (less than 2%) occurred upon cooling. This is in agreement with a S=1/2 system, i.e. the Cu(II) ions are hardly, and if so very weakly, ferromagnetically interacting. The magnetic orbitals of the Cu(II) appear to not overlapping, and this can be the reason for the absence of significant magnetic interaction. The curves of CHI and CHI.T vs T have been redrawn in Figure S5.

3.2 Description of the crystal structure of the title compound

Each Cu^{II} centre is coordinated by a 2,2'-bipyridyl unit occupying one pair of mutually *cis* sites and two independent 1,1,3,3-tetracyano-2-ethoxypropenide (tcnoet) anions, occupying a second pair of mutual *cis* sites; this unit is organized in a dinuclear (dimeric) fashion. The

asymmetric unit with the atomic labeling used is depicted in Fig. 1. Relevant bond lengths and angles are listed in Table 1.

Table 1:

Relevant Bond distances (pm) and angles (deg) for $[Cu_2(\mu\text{-tcnoet})_2(tcnoet)_2(bpy)_2]$

Description	Distances	Description	Angles
Cu-N11 (bpy)	198.78(14)	N11-Cu-N12	81.55
Cu-N21 (bpy)	199.44(14)	N311-Cu-N411	90.41
Cu-N311	199.57(15)	N432-Cu-N11	97.55
Cu-N411	198.74(15)	N432-Cu-N12	91.80
Cu-N312*	233.58(15)	N432-Cu-N311	84.88
Cu-N432#	278.59(18)	N432-Cu-N411	102.37
Cu-Cu	751.3 (dimer) 984.2 (chain)		
* and #	Related by symmetry operations: (-*x* + 1, -*y*, –*z* + 1) and (-*x*, -*y* +1, -*z* +1)		

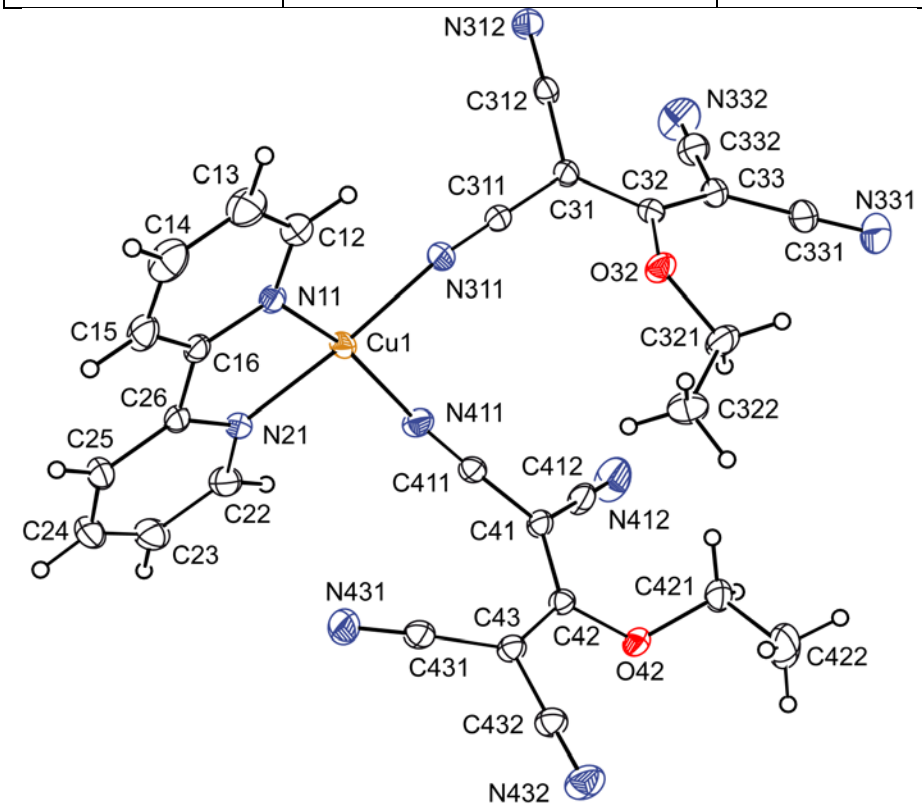


Figure 1: ORTEP representation of the asymmetric unit of the title compound, together with the atom labeling used. Displacement ellipsoids are drawn at the 20% probability level.

The centrosymmetric dinuclear unit with two bridging tcnoet ligands is shown in Figure 2. The Cu---Cu distance is 751.3 pm.

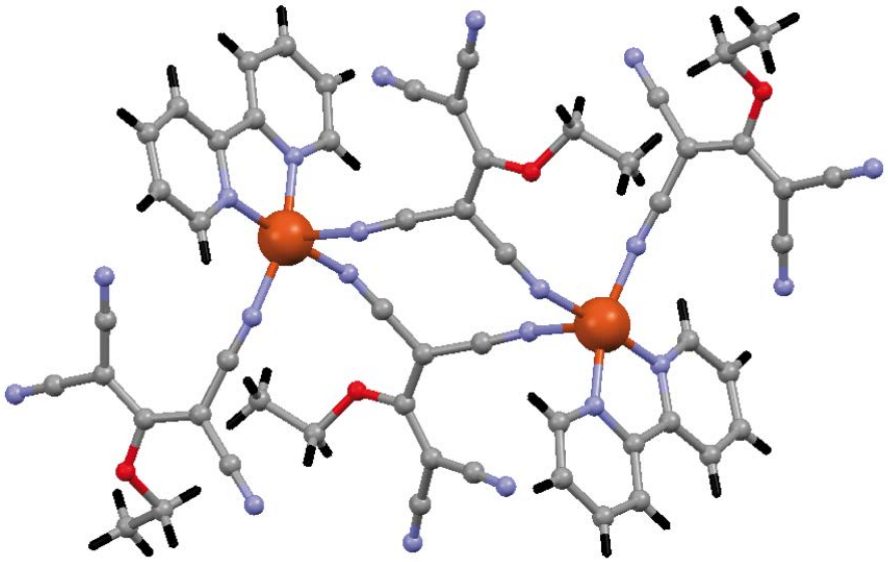


Figure 2. The dinuclear unit showing bridging tcnoet ligands, and the terminal monodentate ligand. Large brown spheres: Cu. Blue: nitrogen; red: oxygen; grey: carbon.

These dinuclear units are further linked up in chains via weak coordination of a sixth ligand, whereby the axially elongated (4 + 2) coordination at the Cu^{II} centre is completed by a further tcnoet ligand. So in fact the Cu^{II} ion has one moderately weak bonding N (N312*) from the bridging ligand in the dinuclear unit (238 pm), and a second, even weaker one ($N432^{\#}$) from a nearby dinuclear unit (279 pm). The distorted geometry of the CuN_6 chromophore for the Cu^{II} is depicted in Figure 3.

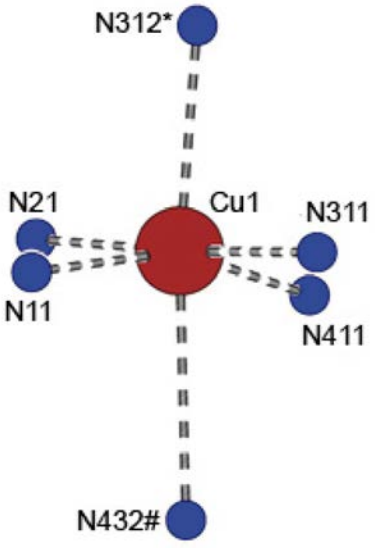


Figure 3: The distorted, axially elongated 4+2 coordination at the Cu^{II} centre: the N atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions (-*x* + 1, -*y*, –*z* + 1) and (-*x*, -*y* +1, -*z* +1), respectively

In fact each tcnoet ligand acts as a bridging ligand between two Cu^{II} centres thereby forming an alternating one-dimensional coordination polymer running parallel to the (1-10) direction in which centrosymmetric 12-membered rings, centered at (0.5 + *n*, -*n*, 0.5) alternate with centrosymmetric 16-membered rings centered at (*n*, 0.5 - *n*, 0.5), where *n* represents an integer in each case (see Figure 4 for a projection of four Cu units of this chain).

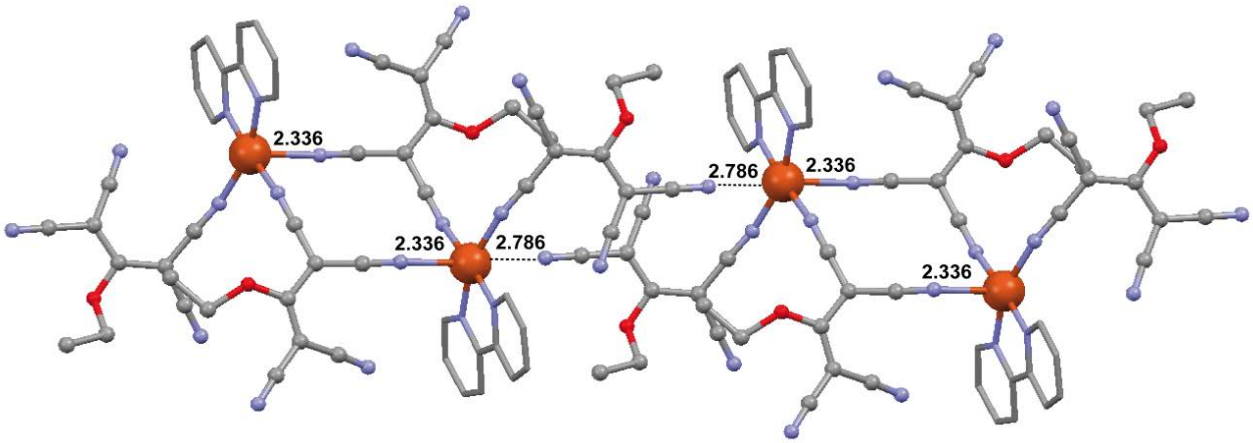


Figure 4: Tetranuclear chain element, where two dinuclear units are linked in chains by a single elongated Cu--N bond (distances of 278.6 and 233.6 pm are marked).

Finally the coordination polymer chains are related by translation along (001) and linked by very weak C-H...N hydrogen bonds (C….N = 369 pm), in a *C*(10) motif [21] to form a sheet lying parallel to (110) thereby generating two further types of centrosymmetric rings (see Figure S6 for a projection). In fact also 12- and 16-membered rings are formed within each coordination polymer chain. Lying between the coordination polymer chains there are 24-membered rings centered at (*p*, 0.5 - *p*, *q*) and 32-membered rings centered at (0.5 - *p*, *p*, *q*), where *p* and *q* represent independent integers in each case**.**

The large chelate ring is slightly non-planar, with a maximum deviation from the mean plane of 52(2) pm for atom N11 and an r.m.s. deviation of 37 pm. Consistent with this is the fact that the two rings of the 2,2'-bipyridyl ligand are not quite parallel, and the dihedral angle between their mean planes is 5.1(2)^{o}. The bond distances and the conformation of the two independent tcnoet ligands are very similar to each other and to those found in an earlier reported compound related compound [10] with , for each ligand, a conrotatory displacement of the two $C(CN)_2$ units from the central C3 propenide plane; the dihedral angles between the $C(CN)_2$ units and the central plane range from 14.0(2)^{o} to 25.5(2)^{o}**.** The electronic delocalisation in this anionic ligand has recently been discussed [10] and needs no amplification here.

Concluding Remarks

The results described and discussed above have shown the synthesis and structure of a remarkable Cu^{II} coordination compound with the anionic ligand tcnoet. The primary organisation of the compounds consists of dinuclear Cu units, held together by 2 (slightly asymmetric) tcnoet ligands. These dinuclear units are further organized in alternating chains, with Cu---Cu contacts of 751.3 and 984.2 pm. These chains are finally organized in layers, via weak bpy-CH....N bonds (C...N = 349.8 pm).

The compound has been further characterized by IR, LF (as solids) and EPR spectra (solid and solution). Despite the polymeric structure, significant Cu-Cu magnetic interactions were not found from a magnetic study down to 4 K. The fact that the magnetic orbitals of Cu^{II} are mutually orthogonal and the quite long Cu-Cu contact distances can explain this behaviour.

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Supplementary information

The crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1012784. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 (0)1223 336033 or Email: deposit@ccdc.cam.ac.uk.

Infrared and ligand field spectra of the title compounds are depicted in the supporting information (Fig S1-S2), together with the powder EPR and a frozen solution EPR (Figs S3-S4). The magnetic susceptibility data are summarized in Figure S5, and a projection of the packing is depicted in Figure S6.

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